



Catalytic steam reforming of biomass tar over iron- or nickel-based catalyst supported on calcined scallop shell

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ABSTRACT

Calcined scallop shell (CS) exhibits alkaline property with a porous structure, and could be applied for the adsorption and decomposition of biomass-derived tar. In this study, steam reforming of tar derived from pruned apple branch over CS was investigated in a fixed bed at 650 °C. It was found that CS had good activity for the steam reforming of tar to produce synthesis gas (syngas), and was able to be recycled. To promote the gas production efficiency, iron or nickel was supported on the CS, and used for the reforming of tar. The effect of heating rate on the gas production rate was investigated, and it was found that reduced iron- or nickel-supported CS showed better activities under the condition of rapid heating. Iron- or nickel-based catalyst in its oxide state was also investigated for the reforming of tar. No catalytic activity was found at the beginning, but good activity appeared after approximately 30 min of reaction when the metal oxide was reduced to its metallic form by the initially generated syngas (CO and H₂) from the pyrolysis of biomass without the aid of catalyst. Iron and nickel in their metallic forms rather than their oxide ones were considered as active sites for the reforming of tar. Furthermore, the alkaline elements in the biomass, which could enhance the activity of the catalysts, were identified to be accumulated on the surface of the catalysts with the biomass-derived tar. As a result, a larger amount of syngas was produced when the regenerated catalysts were applied. Based on these experimental results, a possible catalytic process was proposed.

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1. Introduction

Biomass is considered a CO₂ neutral source of renewable energy. However, biomass has a low energy density, is relatively costly to collect and be converted, and has a limited availability from a geographical and temporal point of view. The production of synthesis gas (syngas) from biomass via gasification is one of the promising thermochemical conversion methods to convert the energy content of biomass into a more practical and clean fuel. Syngas can be used for the production of methanol, ethanol, DME, oxo-chemicals, Fischer and Tropsch fuels, and heat and power [1–3]. However, a large amount of tar is generally generated together with syngas during biomass gasification. Tar is undesirable since it could condense even at relatively high temperatures, resulting

in filter fouling and pipe blockage in the downstream processes [4]. Removal of tar by efficient adsorption and reforming to syngas should be important and indispensable to commercialization of this technology for applications in power generation and synthetic fuel production.

Catalytic reforming of tar at temperatures in the range of 600–900 °C has been widely studied. Many researchers identified that noble metals, nickel and other transition metals supported on alumina and ceramic materials, natural minerals such as olivine and domomites, and biomass/coal-derived char showed good activities for the reforming of tar [3–35]. Noble metal catalysts such as Pt, Rh, and Ru generally show high activities for the reforming of tar, but high loadings of these metals are considered to be unsuitable for practical process due to their high costs [5–7]. In order to reduce cost and improve reforming economics, low loadings (<0.5 wt%) of such noble metals on some special materials such as Mg–Ce–Zr–O mixed-metal oxides were investigated and the catalysts obtained exhibited high catalytic performances at low temperatures and could be considered potential industrial catalyst for the tar steam reforming. Nickel-based catalysts were also

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verified to be active for the reforming of tar at low temperatures [8–13]. Wang et al. [14] converted bio-oil, which included tar, to hydrogen by using commercial nickel-based steam reforming catalysts at 700 °C, and a hydrogen yield of as high as 85% was achieved; the used catalysts were easily regenerated by steam or CO₂ gasification of carbonaceous deposits. Chaiwat et al. [15] found that light tar could be completely decomposed over biomass char at relatively high temperatures of 800–900 °C. Li et al. [16] confirmed that nickel-loaded brown coal char is very active for biomass volatile gasification at relatively low temperatures ranging from 450 to 650 °C. Natural materials such as calcined olivine and dolomites attract much attention as catalysts for tar cracking/decomposition due to the fact that they are cheap and disposable and show high catalytic activity. Swierczynski et al. [17] used natural iron-bearing olivines (Fe_xMg_{1-x})₂SiO₄ as tar-cracking materials in fluidized bed biomass gasification due to its optimal hardness and found that iron present in the olivines significantly influenced its catalytic activity. However, to obtain an olivine with a high activity for the reforming of tar, it is desirable to extract the maximum amount of reducible iron from its structure by thermal treatment under oxidation-reduction conditions. It was found that calcination temperatures as high as 1000–1100 °C were necessary for this purpose. Virginie et al. [18] prepared 10–20 wt% iron loaded olivine catalysts and used them for the reforming of toluene as a tar model compound in a fixed bed reactor at 825 °C, and reported that 91% of toluene was converted. Characterizations performed after the tests indicated that a high percentage of iron in its metallic form, which is beneficial to C–C and C–H bonds breaking, was maintained. Dolomite, which generally consists of 30 wt% CaO, 21 wt% MgO, 45 wt% CO₂, and trace amounts of minerals such as SiO₂, Fe₂O₃ and Al₂O₃, seems to be more active than olivine in the reforming of tar, and is well-known for its CO₂-capture properties. However, the reforming temperature should be over 700 °C [19,20]. Di Felice et al. [21] incorporated iron in calcined dolomite and its constituent compounds, CaO and MgO, for steam reforming of toluene, and found that addition of iron enhanced the activity of pure CaO or pure MgO, but this improvement upon reactivity was absent in Fe/dolomite reactivity. Several studies suggested that iron in its metallic form showed high catalytic activity for tar cracking/reforming, but iron oxides, FeO, Fe₂O₃ and Fe₃O₄ had no catalytic activity [22–24]. However, Uddin et al. [25] believed that Fe₂O₃ possessed catalytic activity in biomass tar gasification at 600–850 °C. Addition of Ce into the catalysts promoted gasification of deposited carbon as well as the water-gas shift reaction, and as a result, the stability of the catalyst was improved [26]. Zhang et al. [27] prepared 3–6 wt% Ni loaded olivine catalysts doped with 1 wt% CeO₂ for the steam reforming of benzene and toluene as tar model compounds in a bench scale fixed bed reactor at temperatures between 700 and 830 °C. It was found that 3 wt% NiO/olivine doped with 1 wt% CeO₂ was the most promising catalyst based on its activity and resistance to coking. Polychronopoulou et al. [28] doped iron catalyst on various support materials prepared by sol-gel and incipient wetness impregnation methods for the steam reforming of phenol (one of the main constituents in tar) at temperatures in the range of 600–700 °C and found that a 5 wt%Fe/50Mg–50Ce–O catalyst showed the highest activity in the production of H₂ with the lowest amounts of accumulated carbonaceous deposits. Addition of other elements such as K, Mn, Cu, Zr or combination of Fe or Co with Ni were also identified to be able to promote the steam reforming of tar [29–33].

Besides calcined dolomites and olivines, calcites could be another attractive natural material for the reforming of tar because it is also inexpensive, non-toxic and disposable, and significantly active at high temperatures [34–38]. Constantinou et al. [34,35] investigated the steam reforming of phenol over a natural

pre-calcined (air, 850 °C) calcite material at temperatures in the range of 650–800 °C, and found that the surface morphology of the CaO derived from the calcinations of calcite played an important role in its reforming activity. The absorption of CO₂ on CaO enhanced water-gas shift reaction, and resulted in a product gas with high hydrogen and low CO content.

A large amount of scallop (*Patinopecten yessoensis*) shells, with main composition of approximately 98 wt% CaCO₃, 0.79 wt% MgCO₃ and 0.15 wt% SrCO₃, are discarded in the northern Japan regions. With the increase in amount year by year of such disposed materials, problems associated with such disposal such as the emission of offensive odors are becoming a concern [39]. In this regard, the possibility of utilizing these waste scallop shells has become an issue for consideration recently. In this study, calcined scallop shells (CS) were applied for the adsorption and steam reforming of biomass-derived tar from pruned apple branch at low temperatures (e.g. 650 °C) in a fixed bed reactor. The results of this study are expected to provide substantial and important fundamental information for their application in the gasification of biomass in future. In order to improve the activity of CS at low temperatures, iron or nickel was loaded on the calcined shells via wet impregnation method and their catalytic activities were investigated.

2. Experimental

2.1. Biomass

In the present study, pruned apple branch of Aomori, Japan was chosen as the biomass sample. A branch was cut into chips with a size of approximately 6 mm × 3 mm × 2 mm and dried at 105 °C for 24 h prior to experiments. When the dried chip was heated at 650 °C for 2 h in argon, approximately 78.8 wt% (dry basis) of volatiles were produced. The ash content of this biomass after calcination at 650 °C for 5 h in air was approximately 1.98 wt%, and its main composition was 86.16 wt% CaO, 6.21 wt% P₂O₅, 3.12 wt% K₂O, 1.34 wt% SiO₂, 1.56 wt% SO₃, 1.34 wt% Fe₂O₃, and 0.27 wt% MnO₂ according to XRF analysis (Energy Dispersive X-Ray Spectrometer, EDX-800HS, Shimadzu).

2.2. Catalyst preparation and characterization

Dried scallop shells were smashed into chips with a size of approximately 4 mm × 4 mm × 2 mm. In order to remove organic matters out of the smashed shell and investigate the change in its structure after calcination, the smashed shell was calcined in air at 600, 800, and 1000 °C for 5 h, respectively. The microstructure and morphology of the calcined shells were characterized with a scanning electron microscope (SEM, S-800, Hitachi, Japan), and structural and compositional analyses were carried out with X-ray diffraction (XRD, Shimadzu, Japan) with Cu K α radiation.

2.5 wt% Fe or Ni loaded CS was prepared by the incipient wetness impregnation method using Fe(NO₃)₃ (Wako, Japan) and Ni(NO₃)₂ (Wako, Japan) as iron and nickel precursors, respectively. After impregnation and drying overnight at 105 °C, the supported catalysts were calcined in air at 650 °C for 3 h before storage and further use. 2.5 wt% Fe loaded on Al₂O₃ (3.18 mm pellets, Alfa Aesar) was also prepared using the same method. Metallic Fe- and Ni-loaded catalysts (hereafter, named as Fe/CS and Ni/CS, respectively), were prepared by reduction of iron- as well as nickel-loaded CS catalysts in 70% H₂ with Ar at 650 °C for 30 min. The catalysts before and after reaction were characterized by XRD and XRF as well. Since metal Fe and Ni were very easy to be oxidized and CS could absorb CO₂ in the air when they are exposed to air, all catalysts before and after reaction were stored in a closed vacuum chamber before XRD analysis.

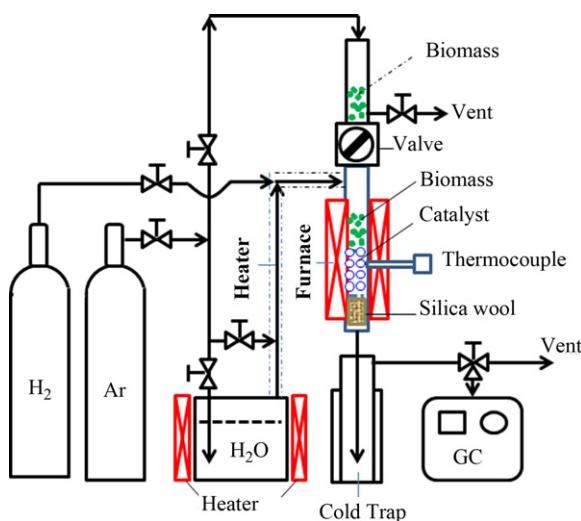


Fig. 1. Schematic overview of the experimental set-up.

2.3. Catalytic steam reforming test

Fig. 1 shows a schematic overview of the setup for the pyrolysis of biomass and steam reforming of tar derived from the biomass. The fixed bed reactor was a quartz tube with an inner diameter of 19 mm and heated with a mullite furnace. Two methods were used to introduce the biomass into the fixed bed: (1) 0.6 g of biomass and 4.5 g of catalyst were separately filled into the fixed-bed reactor with quartz wool, and then the reaction was performed with a heating rate of 5 or 20 °C/min during the test; (2) 4.5 g of catalyst was filled into the reactor and heated to the reaction temperature first, and then 0.6 g of biomass, which was placed in the upper tube and purged with argon in advance, was introduced quickly through a valve above the reactor. (Hereafter, this method will be named as “rapid heating method”.)

Before the test, water was first heated to 90 °C, and then bubbled with 50 cm³/min of Ar gas. Water-saturated Ar ($p_{H_2O} = 70$ kPa) gas was passed through a 120 °C heated tube and flowed into the reactor. The tar, derived from the pyrolysis of biomass placed on the catalyst, was carried by the Ar gas flow and flowed down into the catalyst layer, and reformed with steam over the catalyst. The gases produced were passed through a cold trap and analyzed every 10 min using an online gas chromatograph (Agilent 7890A GC system), in which one TCD with 3 packed columns (1 molecular sieve 5A column + 1 HayeSep Q column + 1 molecular sieve 5A column) was for the separation of CO, CH₄ and CO₂ using He as carrier gas while the other TCD with a molecular sieve 5A for H₂ measurement using Ar as the carrier gas. The remaining char above the catalyst was collected and weighed.

3. Results and discussion

3.1. CS catalyst characterization

Fig. 2(a) shows photographs of scallop shells calcined at different temperatures. One can see that CS became increasingly whiter with the increase in calcination temperature, and became pure white at 1000 °C. **Fig. 2(b)** shows the SEM image of the original scallop shells. Various irregular particles attached on the surfaces of the shell were observed. For scallop shells calcined at 800 °C, as shown in **Fig. 2(c)**, a porous structure was clearly observed on the surfaces, which could be used for the adsorption of tar.

Fig. 3 shows the XRD patterns of CS at different calcinations temperatures corresponding to those in **Fig. 2(a)**. For scallop shell calcined at 600 °C, the main peaks observed were still the characteristic peaks of calcite (CaCO₃). However, peaks of CaO were clearly detected along with the peaks of calcite for the scallop shell calcined at 800 °C, suggesting that a part of the shell had been converted to CaO. All calcite was transformed to CaO for the scallop shell calcined at 1000 °C for 5 h. However, its strength was very weak, and the shell was very easily crushed into powder. On the other hand, CS obtained at 800 °C maintained its original forms, and the remaining

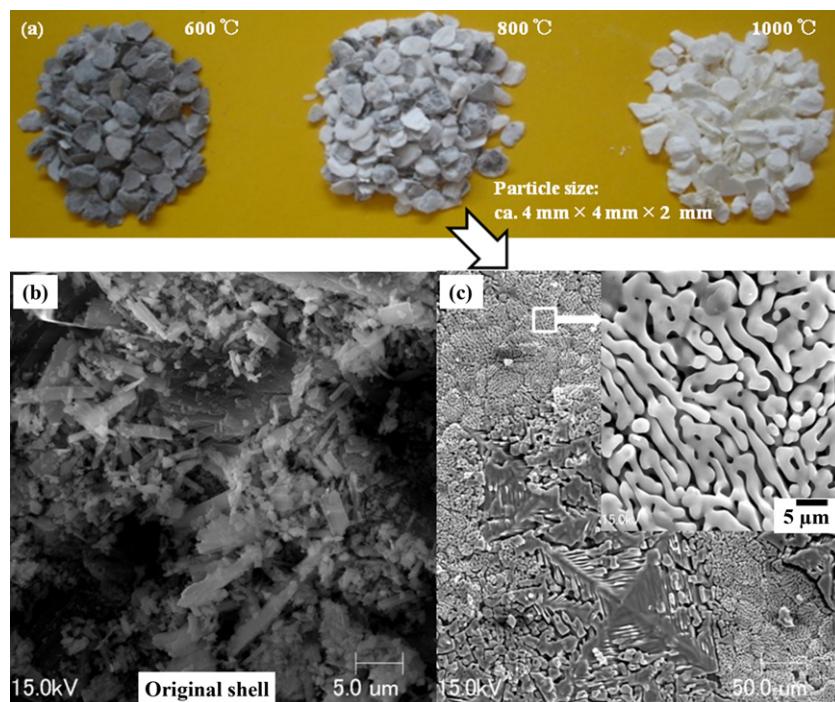


Fig. 2. Images of scallop shells calcined at different temperatures. (a) Photographs; (b) SEM image of the surface of original scallop shell after calcined at 800 °C.

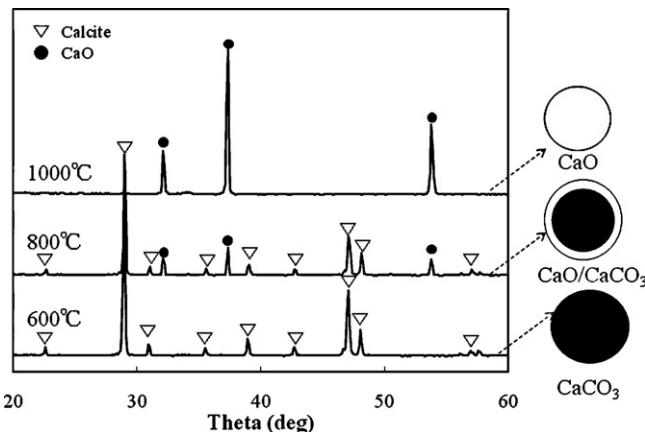


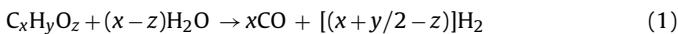
Fig. 3. XRD patterns of CS at different temperatures.

calcite present could enhance the strength of the catalyst. Thus, it was considered to be much more suitable for use as catalyst in the fixed bed. Therefore, in this study, CS obtained at 800 °C was chosen as catalyst and catalyst support for the steam reforming of tar.

4. Catalytic activity of CS

Fig. 4(a) and (b) shows gas production rates at 650 °C as a function of the reaction time when CS was used as catalyst. As shown in Fig. 4(a), when biomass was placed above the CS catalyst, and heated with a rate of 20 °C/min, gas production rates increased rapidly above 600 °C, and peaked after a period when the temperature reached 650 °C. In the present fixed bed, since no continuous feeding of biomass was provided, the amount of tar from the biomass available for reforming should decrease with reaction time. Therefore, after the gas production rate reached a maximum, it decreased with the reaction time. On the other hand, it was possible that carbon deposited on the surface of the catalyst could deactivate the catalyst. However, in the case of the rapid heating method, gases evolved soon after the biomass was introduced, and reached a peak at 20 min, as shown in Fig. 4(b). It should be noted that larger accumulated amounts of the H₂ and CO and less CO₂ were produced over 2 h in the latter case than those in the former case. In the present reforming method, the biomass should be pyrolyzed first, and the generated volatiles moved to the CS surfaces by the carrier gas and reformed by H₂O there. Pyrolysis of wood typically starts at 200–300 °C, and a higher temperature always leads to a higher reaction rate [40]. In the rapid heating method, the volatiles were produced immediately from the biomass when it was introduced into the reactor. Therefore, the gases derived from the reforming of volatiles also evolved much faster than that in the case with low heating rate.

Biomass decomposition and the subsequent reactions among evolved species are very complex [33]. The steam reforming of volatiles derived from biomass can be expressed as the following [21,41]:



The produced CO could further undergo the water gas shift (WGS) reaction due to the excess steam:



Theoretically, the stoichiometric maximum yield of H₂ could be obtained if all carbon contained in the volatiles is completely converted to CO₂. However, Eq. (2) represents reversible reaction, and so the gases detected at the outlet of the reactor always contained CO. In addition, CO₂ and CH₄ are generally produced during

the pyrolysis of biomass and/or tar even without any catalyst. On the other hand, CaO has been used previously to promote the WGS reaction [28,42–44]. In the present study, it is also possible that the absorption of CO₂ on the calcined shell enhanced the WGS reaction during the reaction time. One can see that more CO₂ was produced in the case with low heating rate (as shown in Fig. 4 and Table 1). The tar produced during the heating stage could be adsorbed on the surface of CS and decomposed gradually at higher temperatures. In this case, it should be difficult for the CO₂ produced via the pyrolysis of biomass as well as WGS reaction to come into contact with CS due to the coverage of tar. In general, tar could be reformed with steam more quickly on the surface of CS in the case of rapid heating condition, and in this case, more CS surface could provide for the absorption of CO₂. Hence, less CO₂ and more H₂ were detected.

The CO₂ captured in-situ could react with CaO in the calcined shell, resulting in the formation of CaCO₃, which could deactivate the catalytic performance of the calcined shell. However, at high temperatures, CaCO₃ could be reversibly decomposed to CaO and CO₂. This is a dynamic equilibrium process, which can be predicted from thermodynamic equilibrium theory. In general, this decomposition reaction is favored when CO₂ partial pressure in the product gas is lower than the equilibrium partial pressure of CO₂ ($P_{CO_2,eq}$ is approximately 0.008 atm at 650 °C) [45]. Based on the amount of CO₂ detected during the reaction time in this study, as shown in Fig. 4(d), it was found that the CO₂ partial pressure in the product gas at 650 °C was greater than that of $P_{CO_2,eq}$. Therefore, CO₂ could be captured by CaO if there was enough reaction time to account for mass transfer resistances. However, as shown in the latter section on XRD analysis results (Figs. 12 and 13), the peaks relating to CaO were still observed after the reaction although some of CaO active sites could have been reacted with CO₂.

Fig. 4(c) shows the time profiles of gas evolution when the CS, which had been used in the reforming of tar as indicated Fig. 4(b), was calcined at 650 °C for 1 h in O₂ flow with a flow rate of 50 cm³/min, and reused as reforming catalyst. It can be seen that slightly more syngas was produced. XRF analysis results indicated that a small amount (0.457 wt%) of K₂O, which originated from the biomass as suggested in Section 2.1, existed in the reused CS. In general, biomass contains significant amounts of alkali and alkaline earth metallic (AAEM) species (mainly K, Na, Mg, and Ca). During the pyrolysis of biomass, AAEM species tend to volatilize with the tar [46]. In the present study, a small amount of potassium (K), which is one of the main AAEM species in pruned apple branch, seems to be accumulated on the catalyst layer with the tar with the aid of carrier gas and deposited on the CS. It is known that alkali metals may accelerate the reforming of tar derived from biomass [1–3]. As shown in Fig. 4(b) and (c) and Table 1, a little more H₂ and CO were detected. On the other hand, the accumulation of these AAEM species on the CaO could also enhance the absorption of CO₂, and promote the WGS reaction (Eq. (2)) [28,42–44]. This should be the possible reason why less CO₂ was detected when the CS was reused. However, it should be noted that the promotion efficiency was not too high.

4.1. Catalytic activities of metallic Fe/CS and Ni/CS

Fig. 5(a)–(d) shows production rates of H₂, CO, CH₄ and CO₂ as a function of reaction time, respectively, when metallic Fe/CS and Ni/CS, which were prepared by reduction of iron- as well as nickel-loaded CS catalysts in H₂ for 30 min, were used. One can see that H₂ production rate increased to a great extent compared with the CS, especially in the case of Ni/CS. It was reported that metallic Ni catalysts exhibited much higher reforming activity of hydrocarbons than metallic Fe catalysts [30,48]. This property was caused by the high activation ability of C–H and C–C bond in the hydrocarbon molecules on the Ni metal surface. Furthermore, as

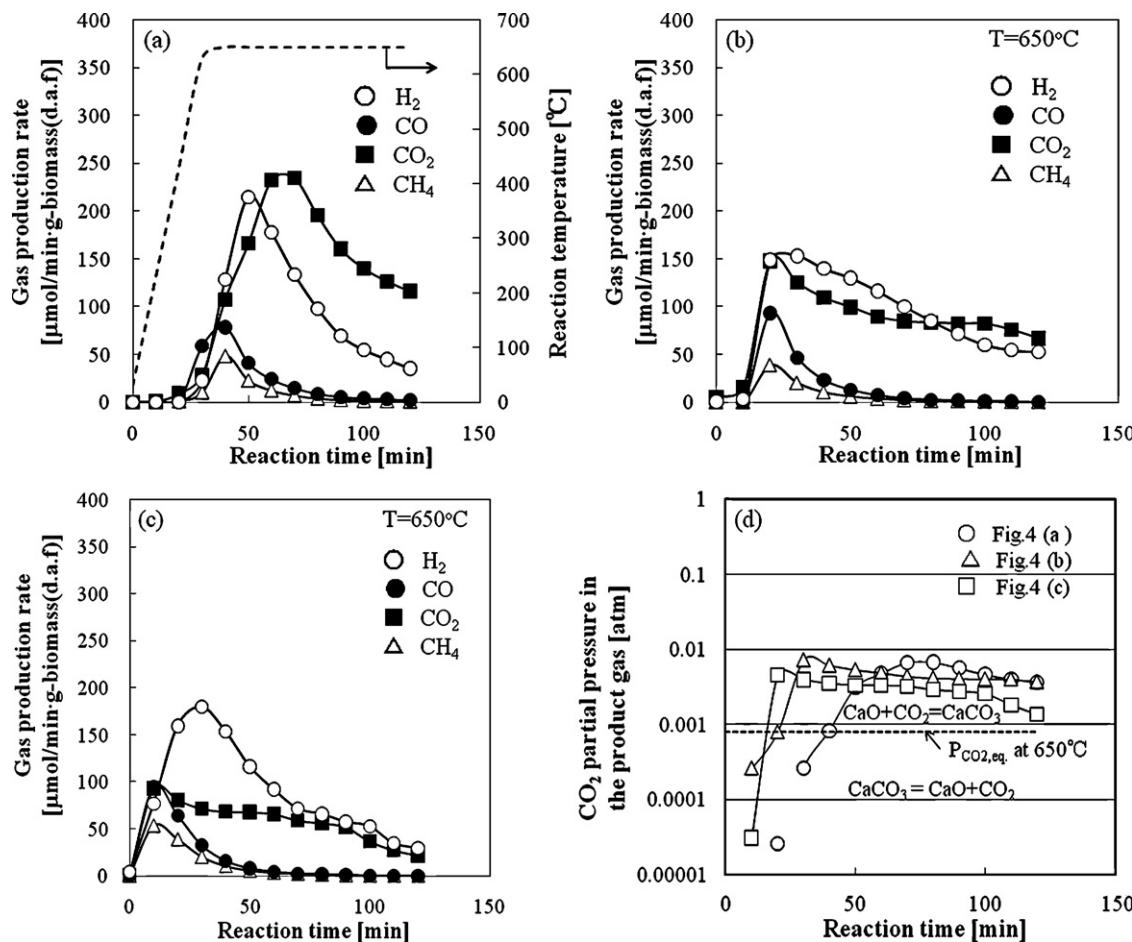


Fig. 4. Gas production rates over CS catalyst at 650°C with (a) heating rate: $20^\circ\text{C}/\text{min}$; (b) rapid heating method; and (c) gas production rates over regenerated CS catalyst corresponding to (b) with a rapid heating method; (d) CO_2 partial pressure in the product gas (CS, calcined scallop shell at 800°C ; carrier gas velocity, $50\text{ cm}^3/\text{min}$; $p_{\text{H}_2\text{O}} = 70\text{ kPa}$).

shown in Fig. 5(b)–(d), no obvious differences for the production of CO, CH_4 and CO_2 were observed for Fe/CS and Ni/CS catalysts. As stated above, metallic iron and nickel have good catalytic activities for the reforming of tar because they are active species for aromatic hydrocarbon destruction, i.e. C–C and C–H bond breakings [1,22,23]. Polychronopoulou et al. [10,11] experimentally proved that the back-spillover process of labile –OH, H and –O species from the MgO, Mg–Ce–O and Mg–Ce–Zr–O support to the Rh and Fe metal surfaces must be considered as true mechanistic reaction path in steam reforming of phenol towards H_2 production. In the present case, the tar could dissociatively adsorb on metal crystallite

sites as well as CS while water molecules are adsorbed on CS surface. H_2 could be produced via dehydrogenation of adsorbed tar and reaction with the back-spillover process of labile –OH, H and –O species from the CS to the metal active sites (as illustrated in Fig. 6).

On the other hand, as stated above, CO_2 could be absorbed on the CS and promote WGS reactions. Fig. 7 shows H_2 , CO and CO_2 evolved over metal Fe catalyst in the presence and absence of CS. In this study, Fe was supported on Al_2O_3 support and reduced in H_2 for 30 min initially. Then, it was physically mixed with CS and SiO_2 beads with a diameter of 1 mm (2:1, w/w), respectively, and used

Table 1
Accumulated gas yields corresponding to Figs. 4 and 5 and 8–11.

Catalyst	Heating rate	Gas yield [$\text{mmol/g}\cdot\text{biomass (d.a.f)}$]				Corresponding to Figure
		H_2	CO	CH_4	CO_2	
CS	$20^\circ\text{C}/\text{min}$	9.8	2.4	1.1	15.2	Fig. 4(a)
CS	650°C	11.2	1.9	0.8	10.7	Fig. 4(b)
CS (regenerated)	650°C	12.3	2.3	1.3	7.1	Fig. 4(c)
Ni/CS	$20^\circ\text{C}/\text{min}$	19.3	2.7	1.3	11.8	Fig. 5
Fe/CS	$5^\circ\text{C}/\text{min}$	8.2	1.6	1.0	3.1	Fig. 8
Fe/CS	$20^\circ\text{C}/\text{min}$	14.2	3.2	1.6	15.6	Fig. 8
Fe/CS	650°C	18.4	4.0	2.0	12.2	Fig. 8
Fe/CS (2nd run)	650°C	16.5	2.7	2.8	11.8	Fig. 9
Fe/CS (regenerated)	650°C	20.7	5.3	2.6	6.3	Fig. 9
$\text{Fe}_{x,y}/\text{CS}$	$20^\circ\text{C}/\text{min}$	13.6	2.9	1.2	12.4	Fig. 10
$\text{Fe}_{x,y}/\text{CS}$	650°C	14.9	4.3	2.8	10.0	Fig. 10
Non-catalyst	$20^\circ\text{C}/\text{min}$	2.6	0.13	0.05	1.56	Fig. 11

d.a.f, dry and ash free.

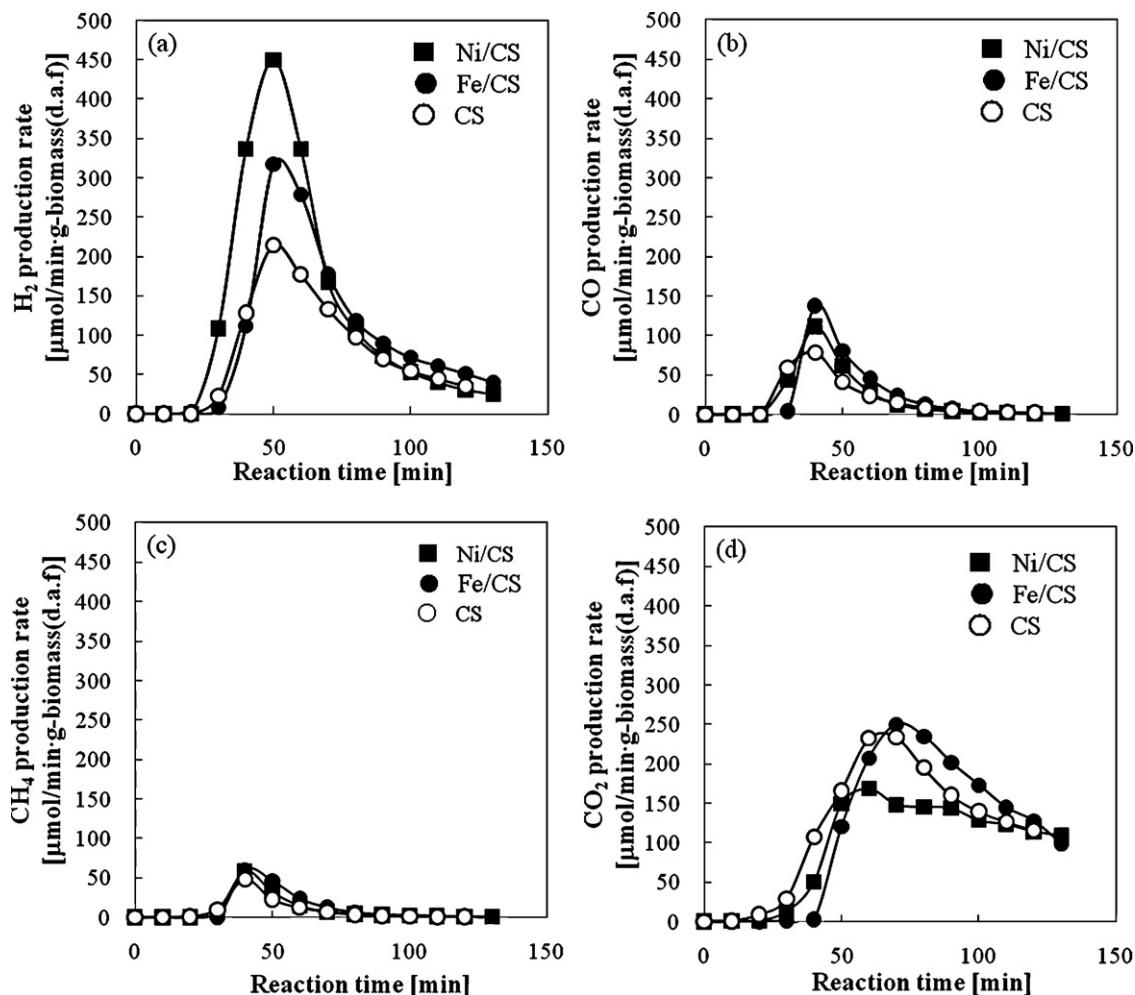


Fig. 5. Comparison of gas production rates over CS, 2.5 wt% Fe/CS and 2.5 wt% Ni/CS at 650 °C. (a) H_2 , (b) CO , (c) CH_4 , and (d) CO_2 (carrier gas velocity, 50 cm^3/min ; $p_{\text{H}_2\text{O}} = 70 \text{ kPa}$; heating rate: 20 $^\circ\text{C}/\text{min}$).

in the fixed bed. One can see that the transient H_2 production in the presence of CS was always larger than that in the absence of CS, especially in the case before H_2 production reached its peak. Furthermore, it was found that the CO_2 detected decreased rapidly after it reached a peak in the absence of CS while the detected CO_2 decreased slowly in the presence of CS. It is possible that the absorbed CO_2 on CS was slowly released at the end of reforming reaction. This phenomenon can be also observed in Figs. 4 and 5. Using phenol as model tar, Polychronopoulou et al. [28] also found that the enhanced production of H_2 occurring in the presence of a CO_2 absorbent material for short times on stream was due to a change in the WGS reaction toward further H_2 production.

Fig. 8(a) and (b) shows the effect of heating rate on the production rates of H_2 and CO over Fe/CS catalyst as a function of

reaction time, respectively. Similar to the results shown in Fig. 4, a rapid heating rate is beneficial for the gas production. If the heating rate is too slow (for example, 5 $^\circ\text{C}/\text{min}$), the volatiles produced by the pyrolysis of biomass at low temperatures (200–500 $^\circ\text{C}$ in

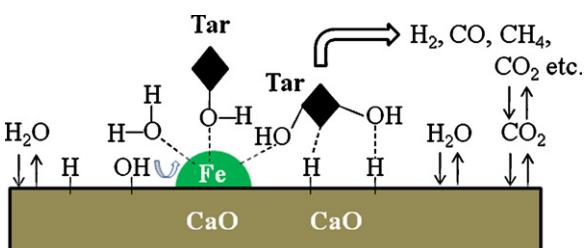


Fig. 6. Adsorption mode of tar, H_2O and CO_2 during the steam reforming of Tar on Fe/CS.

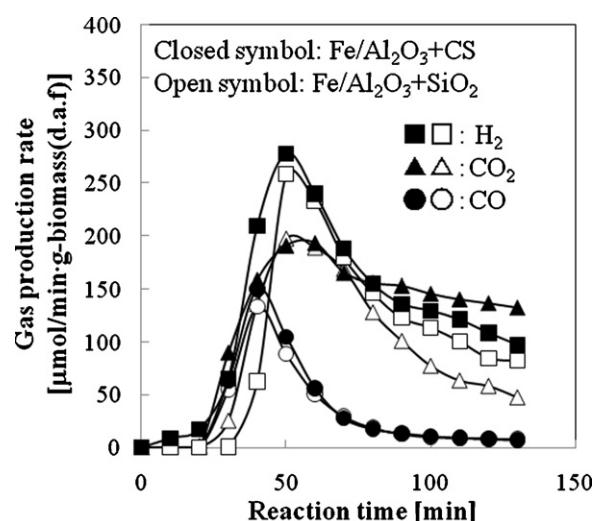


Fig. 7. H_2 , CO and CO_2 evolved over metal Fe catalyst in the presence and absence of CS at 650 °C (carrier gas velocity, 50 cm^3/min ; $p_{\text{H}_2\text{O}} = 70 \text{ kPa}$; heating rate: 20 $^\circ\text{C}/\text{min}$).

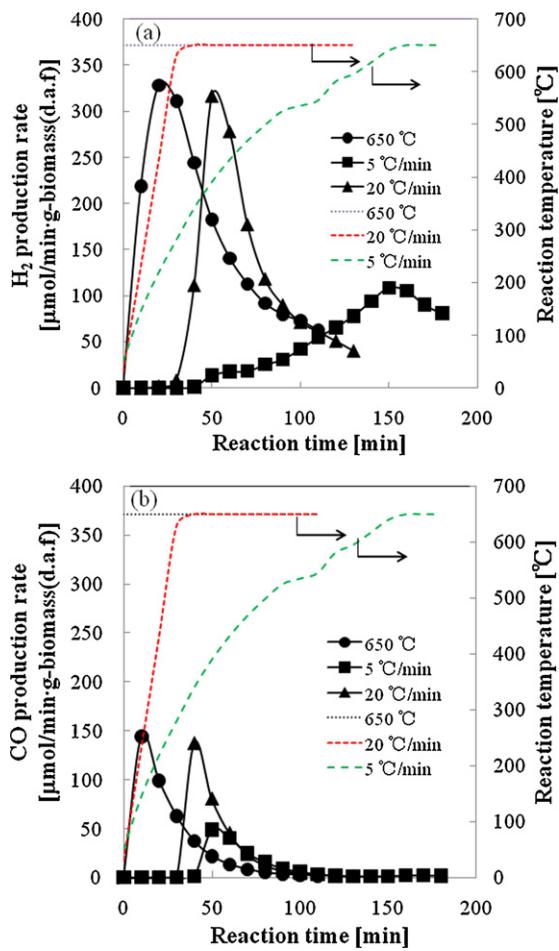


Fig. 8. Effect of heating rate on the production rates of (a) H_2 and (b) CO over Fe/CS catalyst at 650°C (carrier gas velocity, $50 \text{ cm}^3/\text{min}$; $p_{\text{H}_2\text{O}} = 70 \text{ kPa}$).

the present case) could adsorb on and cover the surfaces of Fe/CS. Due to the low catalytic activity of Fe/CS at low temperatures, the H_2 and CO production rates remained low for a relatively long time as shown in the figure. Furthermore, in the case of the slow heating method, the initial tar evolved could be adsorbed on the catalyst, and slowly reformed by steam. The unreacted tar covering on the catalyst could convert into carbon, resulting in the decrease in catalytic activity. In a practical process, it is generally expected that the tar produced is rapidly decomposed and removed from the gas lines. Therefore, the rapid heating method should represent a more realistic approach for steam reforming of the tar.

Fig. 9 shows the stability and reusability of metallic Fe/CS catalyst in the case of the rapid heating method. One can see that the catalytic activity decreased to some extent after the first run for the steam reforming of the volatiles from biomass. Large sized and thermally unstable constitutive molecules such as carbohydrates, furans and phenols are usually contained in the biomass-derived tar. At elevated temperatures, the cracking of such molecules could lead to carbon deposition on the catalyst surface, and reduction of catalytic activities. However, if the used Fe/CS catalyst was calcined at 650°C for 30 min and reduced in H_2 at 650°C for 30 min again, as shown in Fig. 9, the regenerated catalyst showed a better catalytic activity. As stated above, it is also possible that the AAEM species such as potassium which moved from the biomass with the tar to the catalyst promoted the catalytic activity. In fact, minor K_2O (0.587 wt%) was detected in the regenerated Fe/CS with XRF. Similar to the results shown in Fig. 4(b) and (c), a little more H_2 and CO

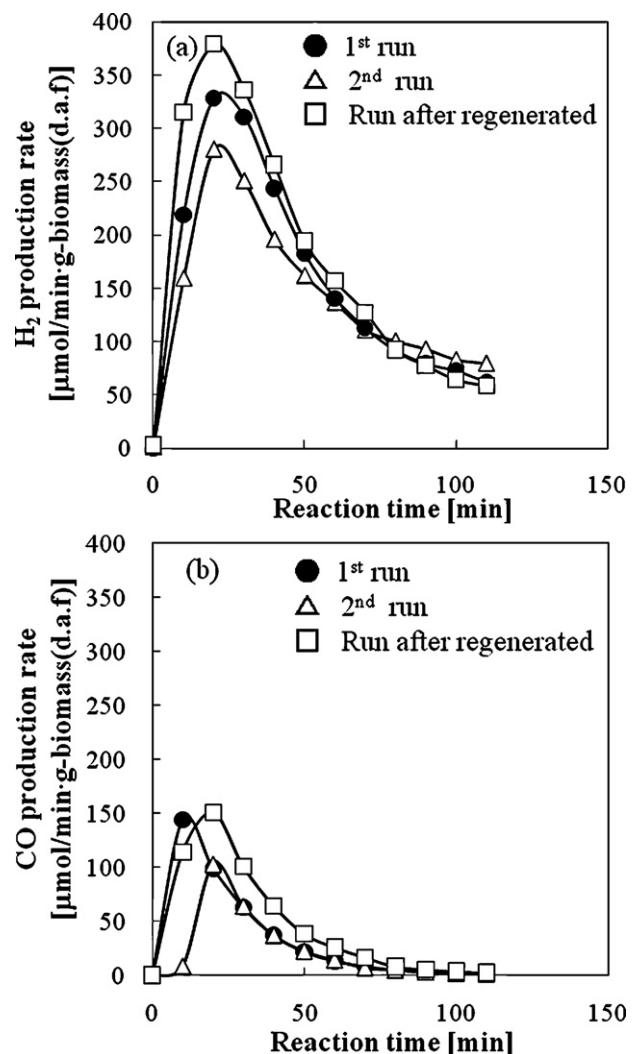


Fig. 9. Stability and reusability of metallic Fe/CS catalyst in the case of rapid heating method. (a) H_2 and (b) CO (carrier gas velocity, $50 \text{ cm}^3/\text{min}$; $p_{\text{H}_2\text{O}} = 70 \text{ kPa}$).

and less CO_2 were detected when the regenerated Fe/CS was used (as indicated in Fig. 9(b) and (c) and Table 1).

4.2. Catalytic activities of $\text{Fe}_x\text{O}_y/\text{CS}$ and NiO/CS

Fig. 10(a) and (b) shows H_2 and CO production rates as a function of the reaction time, respectively, when as-prepared iron oxide loaded CS ($\text{Fe}_x\text{O}_y/\text{CS}$) was used as catalyst. In the case of either the rapid heating method or slow heating method, in comparison with Fe/CS catalyst, it was found that the time of H_2 and CO evolution was approximately 30 min later than that when Fe/CS was used, suggesting that $\text{Fe}_x\text{O}_y/\text{CS}$ began to show catalytic activity for the steam reforming of the volatiles only after a certain period of reaction. A similar phenomenon was also observed when NiO/CS was used for the steam reforming of the volatiles derived from biomass. Although the catalytic activity appeared at a later time, a comparable amount of syngas was also produced in this case. As shown in Fig. 11, if no catalyst was used, a small amount of CO and H_2 also evolved at an earlier stage. It has been proven that CO and H_2 can be produced via biomass self-gasification because biomass contains a number of AAEM species that could act as catalysts in the process [47,49]. Hence, it is inferred that CO and H_2 derived from the pyrolysis of biomass at the earlier stage could act as reducing agents to convert a part of Fe_xO_y on the CS to the metallic state, resulting in

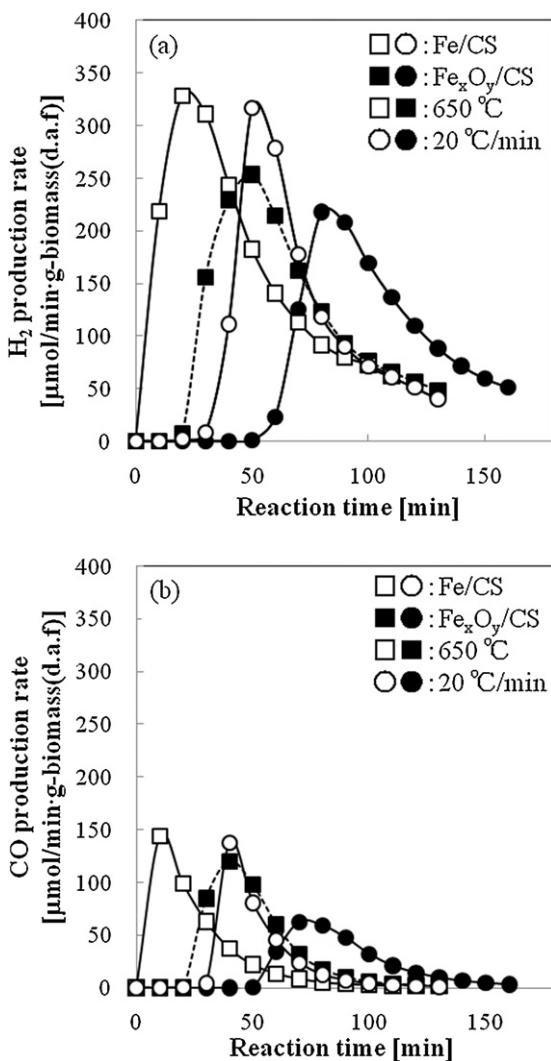


Fig. 10. H₂ (a) and CO (b) production rates as a function of reaction time over Fe_xO_y/CS catalyst with different heating rates (carrier gas velocity, 50 cm³/min; p_{H2O} = 70 kPa).

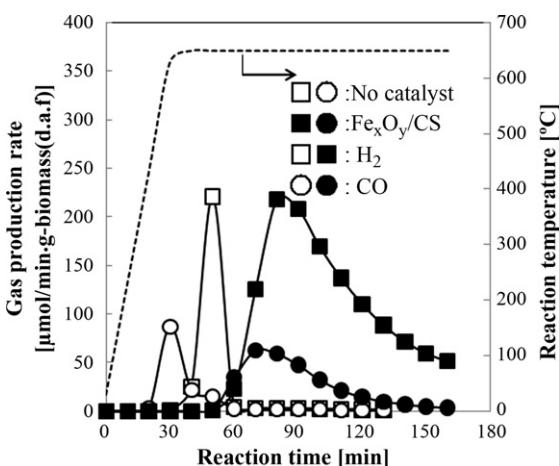


Fig. 11. The moments of H₂ and CO production in the cases without catalyst and with Fe_xO_y/CS catalyst.

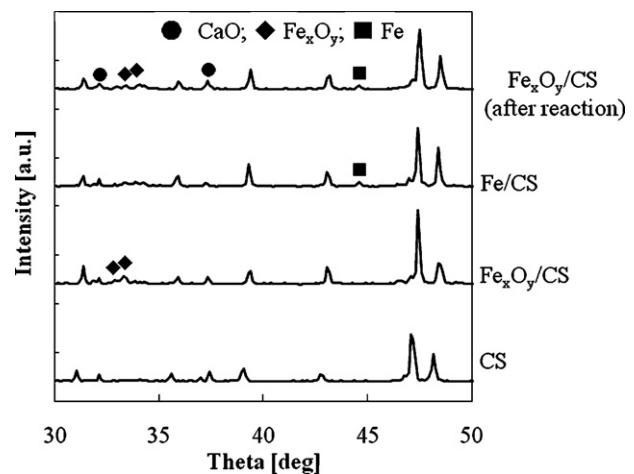


Fig. 12. XRD patterns of Fe_xO_y/CS before and after the reaction.

the appearance of the catalytic activity. The further generated CO and H₂ over Fe/CS could help to maintain such catalytic activities until the reaction was completed.

Fig. 12 shows XRD patterns of Fe_xO_y/CS before and after the reaction. A small peak corresponding to metallic iron was clearly seen on the XRD of the catalyst after reaction, suggesting that a part or all of the iron oxides could be converted to metallic iron during the reaction. It should be noted that metallic iron is very easy to be oxidized in air. Hence, it is very important to keep the spent catalyst in an inert environment in order to obtain its XRD pattern correctly. Similar result was also obtained for NiO/CS. As shown in Fig. 13, the peak corresponding to metallic Ni was clearly observed on the XRD pattern of the catalyst after reaction. Therefore, although some researchers considered that iron oxide such as Fe₂O₃ could act as catalyst for the reforming or cracking of tar [25], the catalytic activity should only be present when the iron- or nickel-loaded catalyst is in its metallic state.

Fig. 14 compares gas yields when different catalysts were used. When no catalyst and steam was used, very low gas yields were obtained. It should be noted that approximately 395 mg-tar/g-biomass was produced in this case based on the tar collected by 30 ml of isopropanol. H₂ yield increased by 4.0 times with CS, 6.6 times with Fe/CS, 5.3 times with Fe_xO_y/CS, 6.9 times with Ni/CS, and 6.3 times with NiO/CS at 650 °C for a 2 h reaction when compared

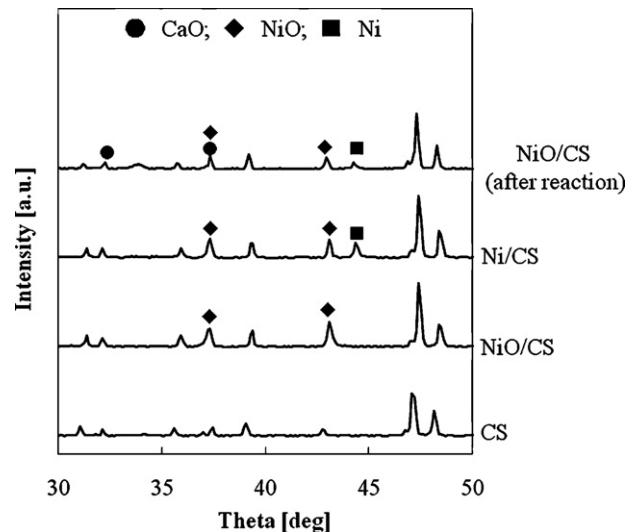


Fig. 13. XRD patterns of NiO/CS before and after the reaction.

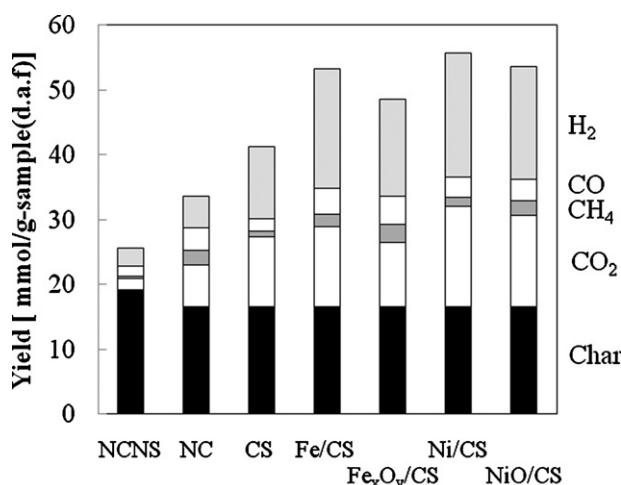


Fig. 14. Comparison of gas yields over different catalysts in 2 h at 650 °C (NCNS, no catalyst and no steam; NC, no catalyst).

with the case of no catalyst and no steam. It should be noted that a large amount of gases were also produced when metal oxide loaded catalysts were applied directly. Table 1 summarizes the accumulated gas yields in Figs. 4 and 5 and 8–11. One can see that (1) more H_2 and CO and less CO_2 were produced over Fe/CS as well as $\text{Fe}_x\text{O}_y/\text{CS}$ under rapid heating condition than those under low heating rate condition; (2) more H_2 and CO and less CO_2 were evolved over regenerated CS as well as Fe/CS than those over the fresh ones.

4.3. Process aspects of steam reforming of the volatiles and tar derived from biomass over metal oxide-loaded CS

It is possible to summarize the process aspects of steam reforming of the volatiles and tar derived from biomass over metal oxide-loaded CS using Fig. 15 based on the above results. In this study, biomass was separately set above the catalyst. When the reaction temperature was increased to 200–400 °C [40,50,51], H_2 and CO were generated by pyrolysis of biomass, and moved by the carrier gas to the surfaces of $\text{Me}_x\text{O}_y/\text{CS}$ ($\text{Me} = \text{Fe}$ or Ni). Part of the Me_xO_y on the CS was reduced to a metallic state. As a result, the tar reaching the catalyst layer could be reformed to gases by the steam on the active metallic sites. The H_2 and CO produced had a reductive nature that could maintain the catalytic activity of the metallic elements until the reaction was completed. Simultaneously, a part

of the AAEM species such as potassium could be moved to the catalyst layer with the volatiles, and deposited on the catalyst after the volatiles were reformed. These AAEM species could promote the catalytic ability of Me/CS to some extent if the catalyst was reused. On the other hand, as stated above, enhanced production of H_2 could occur due to a change in the WGS reaction toward further H_2 production via the absorption of CO_2 on the CS during the reforming reaction.

5. Conclusions

Steam reforming of the volatiles and tar derived from pruned apple branch over calcined scallop shell (CS) as well as iron- or nickel-loaded CS was investigated in a fixed bed reactor at low temperatures. The main results of this study can be concluded as follows:

- (1) CS showed alkaline property with porous structure and it had good activity for the steam reforming of the volatiles and tar derived from pruned apple branch to produce syngas, and was recyclable.
- (2) Reduced iron- or nickel-supported catalysts showed much better activity than CS. Heating methods had a significant effect on gas production rates. Larger volumes of gases were produced under the condition of rapid heating rates.
- (3) Iron- and nickel-supported catalysts in their oxide states were also investigated for the reforming of tar. No catalytic activity was found at the beginning of the reaction, but good activities appeared after a period of reaction when the metal oxides were reduced to their metallic forms by the syngas (H_2 and CO) initially produced from the pyrolysis of biomass without the aid of the catalyst. Iron and nickel in their metallic forms rather than their oxide forms were considered the active sites for the reforming of the volatiles and tar.
- (4) The enhanced production of H_2 due to a change in the WGS reaction toward further H_2 production via the absorption of CO_2 on the CS during the reforming reaction was identified.
- (5) AAEM species in the biomass, which could promote the activity of the catalysts, were identified to be accumulated on the surface of the catalysts with the biomass-derived volatiles and tar. As a result, larger amounts of syngas were generated when the regenerated catalysts were used.
- (6) Based on these experimental results, a possible catalytic process was proposed to explain the catalysis phenomenon when metal oxide loaded CS was used.

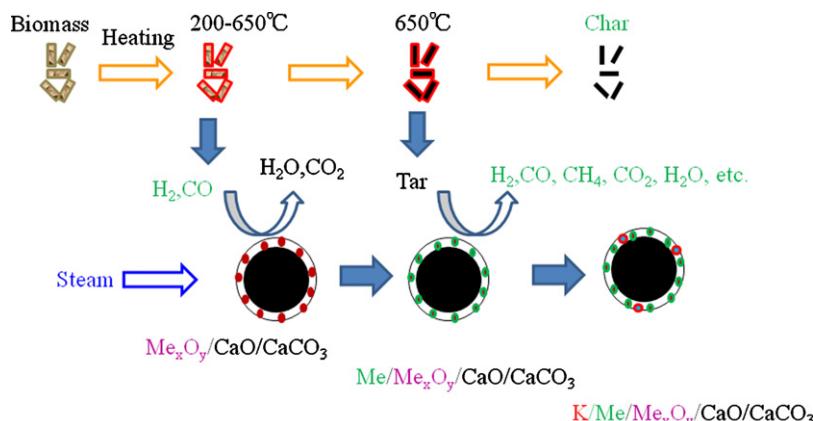


Fig. 15. Schematic representation of catalytic process aspect of $\text{Me}_x\text{O}_y/\text{CS}$ ($\text{Me} = \text{Fe}$ or Ni) for the steam reforming of the tar derived from biomass.

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